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FUNCTIONAL GLASS CERAMIC BASED ON POTASSIUM NIOBATE

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A new approach to obtaining a functional glass ceramic based on potassium niobate from an amorphous precursor, obtained by rapid cooling of the melt containing small additions of the glass former SiO_2, is examined. The results indicate that there is promise in the glass ceramic technology, which ensures the formation of cubic $KNbO_3$ crystals of almost ideal habitus whose flat grains surrounded by thin, composition-regulated glass interlayers can stick to one another. The ceramic $KNbO_3$ obtained by the glass ceramic technology differs beneficially from its conventional analog by low tanä in the entire range of existence of the ferroelectric phase (below 410°C), which determines its advantage for a host of applications.

Key words: alkali-niobium silicate glasses, potassium niobate, piezoelectric ceramic.

A great deal of attention is now being focused on finding new compositions and developing methods for obtaining a lead-free piezoceramic as an alternative to lead zirconate-titanate (LZT) that is more attractive from the environmental standpoint [1, 2]. The proposed compositions must satisfy a number of requirements, the most important being high spontaneous polarization P_s of the ferroelectric and high values of the associated coefficients of longitudinal d_{33} and transverse d_{31} piezoelectric effects, low dielectric losses ($\tan\delta < 0.01$) and a wider utilization temperature range, bounded for LZT by sharp growth of the electric conductivity at 150 – 180°C. The best piezoelectric characteristics obtain when the tetragonal and rhombohedral phases of the system $(1 - x)PbZrO_3 - xPbTiO_3$ with $x \sim 0.52 - 0.53$ in the so-called morphotropic region coexist in the ceramic. The Curie temperature, equal to about 280°C near $x = 0.5$, above which the ferro-, piezo-electric properties vanish, imposes a fundamental limitation on the working temperature range of LZT.

The perovskite-like ferroelectric potassium niobate $KNbO_3$ is a close structural analog of lead titanate and possesses a high spontaneous polarization 25 – 30 $\mu C/cm^2$. The morphotropic region based on $KNbO_3$ is realized as coexistence of tetragonal and rhombic phases in the system $(1 - x)KNbO_3 - xKNbO_3 - yMSbO_3$ with $x \sim 0.5$, $y \sim 0.05$ and $M = $ Li or Ag [3], where Nb can be replaced by up to 20 at.% Ta [2].

The potassium niobate based ceramic compositions indicated above are considered to be competitive with respect to conventional LZT compositions which they will be able to replace successfully in a number of technical applications, provided that an appropriate technology is developed. The $KNbO_3$ based piezoceramic differs beneficially by its lack of the environmentally dangerous lead component and by its usability at elevated temperature to 250 – 300°C. The latter property is due to the highest (after lead titanate) ferroelectric Curie temperature in the perovskite family, which in the case of pure $KNbO_3$ is 410°C [4].

The proneness of polycrystalline potassium niobate toward recrystallization at temperatures near the incongruent melting point (1040°C) together with inadequate sinterability at low temperature impedes the attainment of high density and uniformity of the $KNbO_3$ based ceramic obtained by the conventional ceramic technology. Usually, different oxide and fluoride additives (for example, LiF [5]) are used to improve sinterability, but they promote only weakly the formation of crystalline grains with a regular shape and an ordered arrangement with respect to one another. The use of sintering additives and optimization of sintering regimes enabled the authors of [2, 5] to obtain a $KNbO_3$ based ceramic with density to 95%.

Usually, crystalline grains with the cubic faceting characteristic for perovskite crystals form the most regular microstructure of perovskite-like ceramic. The correspond-

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TABLE 1. Batch Compositions for Obtaining Melts

Composition	Content, mol.%			
	K_2O	Nb_2O_5	SiO_2	B_2O_3
KNS-1	25	25	50	–
KNS-2	27	27	46	–
KNS-3	30	30	40	–
KNS-4	35	35	30	–
KNS-5	40	40	20	–
KNS-6	42.5	42.5	15	–
KNS-7	45	40	15	–
KNS-8	45	45	10	–
KNS-9	47.5	47.5	5	–
KNS-0	50	50	0	–
KNB-1	32	32	–	36
KNB-2	43	21	–	36
KNB-3	50	25	–	25
KNB-4	48	32	–	20
KNB-5	54	27	–	19
KNB-6	41	41	–	18
KNB-7	50	35	–	15
KNB-8	45	45	–	10
KNP-1*	41	41	–	–
KNP-2**	45	45	–	–
KN-1	50	50	–	–
KN-2	53	47	–	–

* Also contains 18% P_2O_5.

** Also contains 10% P_2O_5.

ing precursors for sintering are obtained by "soft chemistry" methods, which include sol-gel processes, currently widely used intensively, as well as hydrothermal synthesis.

Among the methods of obtaining ceramic the crystallization of supercooled melts (glasses) has not been studied adequately. In order to implement this method for metal oxides two problems must be solved: these oxides must be obtained in an amorphous state and the conditions for controlled crystallization of glass simultaneously in the entire volume must be determined.

Rapid cooling of melt makes it possible to obtain amorphous $KNbO_3$ [6] predominately in the presence of glassy components in the melt which affect the subsequent crystallization differently. The existing information on the precipitation of a perovskite-like $KNbO_3$ phase as the first crystallizing phase from glass is contradictory and refers predominately to systems with a high content of the glass former. Thus, T. Komatsu, et al. [7] reported on nanocrystallization of potassium niobate in glasses in the system K_2O–Nb_2O_5–TeO_2 for compositions with a large potassium excess. The quality of the $KNbO_3$ phase was very low, which can be judged by the appearance of the x-ray diffraction patterns presented in this work. The content of the glass former (TeO_2) in the glasses obtained was at least 50%.[5]

The crystallization of glasses in the systems $K_2O(Na_2O)$–$Nb_2O_5(Ta_2O_5)$–$SiO_2(B_2O_3)$ in [8 – 10] was studied for glass former content at least 20 – 45%; $KNbO_3$ precipitation was found only in the silicate system. In this system the precipitation of the phase $KNBSi_2O_7$ was recorded with high silica content and the phases $K_3Nb_3Si_2O_{12}$ and $K_4Nb_6O_{17}$ with low silica content. Studying the products of crystallization of the glasses K_2O–Nb_2O_5–SiO_2 with decreasing amounts of the glass former SiO_2, H. Tanaka, et al. [8] observed $KNbO_3$ formation while casting glasses with 17 – 30% SiO_2, the amount of the $KNbO_3$ phase increasing sharply with decreasing silica content. Intense formation of potassium niobate occurred when two conditions were satisfied simultaneously: large excess of niobium atoms compared with silicon (i.e., large ratio Nb_2O_5/SiO_2) and excess potassium ($K_2O/Nb_2O_5 > 1$). Nonetheless, the amount of the residual glass phase in these crystallized glasses was at least 40%, which is not acceptable for obtaining good ferroelectric properties and determines, specifically, the comparatively weak second-harmonic generation signal (SHG) signal obtained from the sample: about 235 quartz standard units versus the usual value for a powdered sample 2000 – 5000 α-quartz units.

The compositions studied in our recent work, where the glass former is absent or its amount has been reduced to a minimum, are of greatest interest for obtaining material with sharply pronounced ferroelectric properties [11, 12].

GLASS FORMATION AND CRYSTALLIZATION OF $KNbO_3$ WITH B_2O_3, SiO_2 AND P_2O_5 ADDITIONS

To obtain glasses in the systems M_2O–Nb_2O_5–B_2O_3, M_2O–Nb_2O_5–SiO_2 and M_2O–Nb_2O_5–P_2O_5 blanks were prepared either by mixing or sintering powered reagents and then melted in platinum or corundum crucibles.

Chemically pure K_2CO_3, Nb_2O_5, SiO_2, H_3BO_3 and $NH_4H_2PO_4$ were used as the initial components for making glass, depending on the chemical composition. Each batch portion was sufficient for 30 – 40 g of glass. The initial components were weighed on an analytical balance and mixed in a corundum mortar. To obtain the best agreement between the prescribed and actually obtained compositions of the glasses the amount of the most volatile components of the batch were determined experimentally and taken into account. The mass of the volatilized matter was determined as the difference of the mass of the crucible with the computed amount of glass and the actual mass of the crucible with the glass made. The composition of the weighed amounts for preparing melts is indicated in Table 1.

The melting temperature was varied in the range 1350 – 1490°C depending on the type and content of the glass former. The maximum melting temperatures corresponded to

[5] Here and below, the molar content unless otherwise stipulated.

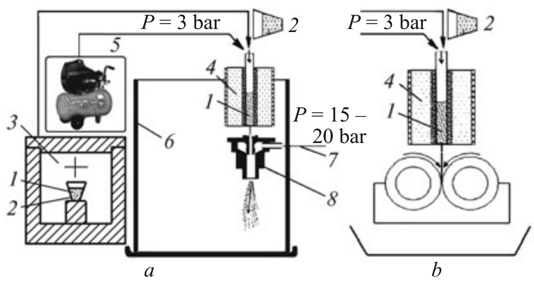

Fig. 1. Scheme for obtaining amorphous materials by blowing on melt (*a*) and rolling with rollers (*b*): *1*) molten glass melt; *2*) platinum crucible; *3*) electric furnace for melting glass; *4*) feeder furnace; *5*) compressor; *6*) collector for the products of blowing; *7*) compressed gas; *8*) coaxial nozzle.

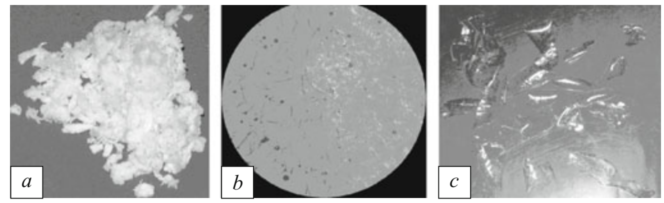

Fig. 2. Molten glass with the composition KNS-9, obtained by different methods: *a*) fiber glass mass obtained by melt blown in a nozzle; *b*) glass material obtained by melt blown in a coaxial head (magnification ×200); *c*) glass in the form of pieces of thin ribbon after rolling melt in rollers and taken from a partially crystallized mass.

the compositions $(1 - x)KNbO_3 - xSiO_2$ with $x > 0.3$. Borate glasses with analogous compositions were made at temperatures 1350 – 1400°C.

Three methods were used to obtain glass from melt by quenching:

1) pouring melt at the making temperature onto a metal plate and pressing with another metal plate to thickness less than 1 mm;

2) blowing with dry air under pressure to 8 atm;

3) pouring melt between two rotating metal rollers.

The methods 2 and 3 were found to be most effective (Fig. 1). For a number of compositions these methods gave almost complete stabilization of the amorphous phase. According to [13, 14], melt cooling rates at least to 10^5 K/sec were characteristic for these methods.

Figure 2 shows an exterior view of potassium niobate based amorphous materials with different compositions, obtained by blowing melt with a high-speed gas flow (*a*, *b*) and quenching in rollers (*c*).

The glass material obtained by the method 2 comprises a finely disperse fiber mass in which the fiber length is 20 – 100 μm and the typical diameter 3 – 5 μm (see Fig. 2*b*). Glass fiber prepared in this way can be used without additional separation to fabricate volume samples of glass ceramic. A uniaxially ordered arrangement of fibers in a blank also creates conditions for uniaxially textured crystallization. The amorphous powder obtained by comminuting glass fiber can be used to prepare ceramics.

Rolling melt in rollers (roller diameter 60 mm, rotation rate 200 – 500 rpm) resulted in stabilization of transparent glass in the form of scraps with thickness 20 – 100 μm for all experimental compositions right up to pure $KNbO_3$ (see Fig. 2*c*). After comminution into powder all amorphous material in the form of ribbings or fibers was used to study the conditions of crystallization of the perovskite phase and to obtain ceramic based on it.

An advantage of both types of raw materials is the complete absence of internal porosity, usually arising because of the agglomeration of microcrystallites.

The powders obtained by methods 2 and 3 were studied after heat-treatment and in the initial state by x-ray diffraction using a DRON-3M diffractometer (CuK_α, Ni filter). The SHG method, specially modified to reveal crystalline phases with non-centrosymmetric structure, was used to reveal the ferroelectric perovskite modification $KNbO_3$ [15, 16]. The SHG signal was determined as the ratio of the SHG intensity in the sample to the SHG intensity in a standard α-quartz powder, after which the quartz standard was used as the basic unit. The method was used to find microquantities of the $KNbO_3$ phase at different stages of crystallization of the glasses and to determine the relative amount of this phase after complete crystallization of the glass.

A temperature study of SHS on crystalline powders made it possible to control the formation of the ferroelectric properties according to the temperatures of the ferroelectric phase transitions. The position and temperature smearing of the phase transitions compared with standard $KNbO_3$ served as an indication of the deviation of the composition and disruption of the structural uniformity of the ferroelectric obtained from the standard $KNbO_3$, for which the transition temperatures are 410°C (cubic-tetragonal phase) and 220°C (tetragonal-orthorhombic phase).

None of the methods 1 – 3 permitted obtaining samples of uniform glass in the potassium-niobium-borate and potassium-niobium-phosphate systems: quenching of the melts KNB-6 and KNB-7, just as KNP-2, led to predominately crystallized material, where the perovskite-like phase $KNbO_3$ was not observed.

The powder diffraction patterns of the glasses KNS-1, KNS-2 and KNS-3, heat-treated at 1050°C for 90 min, contain peaks corresponding to the non-centrosymmetric phases $K_3Nb_3O_6Si_2O_7$ ($K_3Nb_3Si_2O_{12}$) and $KNbSi_2O_7$, dominating over $KNbO_3$. Heat-treatment of these glasses for several hours at temperatures below 700°C gives poorly formed crystalline phases and $K_4Nb_6O_{17}$ phases with layered structure. As a rule, the SHG effect for samples treated at low temperatures is absent or very weak. In this respect the silicate glasses with low SiO_2 content are exceptions. Heat-treatment of the glasses KNS-5 – KNS-9 in the range 650 – 950°C shows a clear tendency toward crystallization

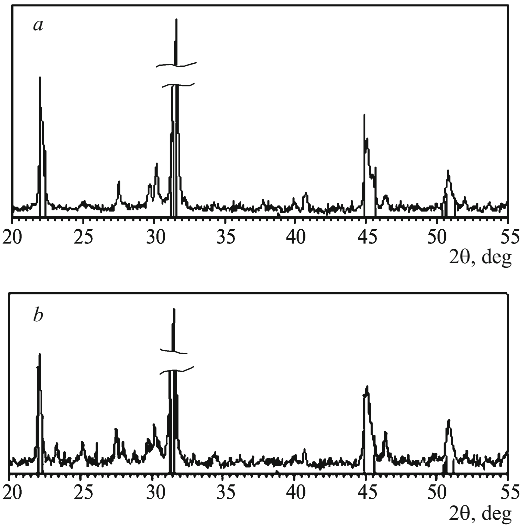

Fig. 3. X-ray diffraction patterns of the glasses KNS-8 (*a*) and KNS-9 (*b*), heat-treated at 950°C for 90 min after quenching on a plate, against the background of the line diagram for $KNbO_3$.

of $KNbO_3$, which is realized even in the process of casting melt onto a plate with direct formation of an opaque crystallized fraction. The best result of formation of the perovskite-like phase $KNbO_3$ was obtained for heat-treated glassy fractions KNS-8 and KNS-9 (Fig. 3), where this phase dominates after heat-treatment.

It follows from the data obtained by x-ray phase analysis that in the case where glass with 5% SiO_2 crystallizes phases based on silicon oxide and potassium niobate K_4NbO_{17} crystallize simultaneously in the interval between the vitrification temperature and precipitation temperature of the $KNbO_3$ phase. Apparently, the remaining potassium above stoichiometry K : Nb = 1 : 1 becomes incorporated in the zeolite-like phase SiO_2 : K with the structure of the mineral ferrierite. In order to identify it reliably in an x-ray diffraction pattern the samples must be annealed for at least 20 h at 600 – 650°C. Low-temperature annealing of the glasses KNS-1 – KNS-9 does not lead to crystallization of the perovskite-like $KNbO_3$, but the introduction of only 1.5% SiO_2 into $KNbO_3$ sharply improves the glass-forming properties of the melt, raising the vitrification temperature of the glass by 120°C compared with amorphous potassium niobate. The low-temperature endo effects in the DTA curves correspond to the crystallization of the zeolite phase SiO_2 : K and metastable phases of potassium niobate. The temperature exo effect corresponding to the crystallization of the ferroelectric $KNbO_3$ [3] shifts from 560°C for the composition with $x = 0$ into the range above 800°C even with the introduction of only 1.5% SiO_2 into the melt and then slowly increases. For this reason the crystallization of the perovskite phase $KNbO_3$ into KNS-9 and glasses with close compositions can occur at 850 – 900°C.

TABLE 2. Compositions, Sintering Regimes and SHG Signal Values for Ceramic Samples with the Composition KNS-9, Prepared Using LG and LiF Additives

Sample	Composition and mass fraction of the sintering additive, %		Sintering regime	SHG, quartz standard units
	LG	LiF		
1	4	–	1040°C (4 h)	2400
2	–	–	1040°C (2 h)	5000
3	4	–	1040°C (2 h)	4600
4	–	–	700°C (4 h) + 1040°C (2 h)	3400
5	1	–	700°C (4 h) + 1040°C (2 h)	3900
6	–	0.5	700°C (4 h) + 1040°C (2 h)	3500
7	–	1	700°C (4 h) + 1040°C (3 h)	3300

OBTAINING $KNbO_3$ CERAMIC

The ceramic was obtained by sintering in electric furnaces of amorphous precursors KNS-9 which were ground in a mechanical mortar, pelleting of powder under pressure to 100 atm and sintering at temperature to 1050°C. The ferroelectric (FE) modifications of $KNbO_3$ were determined by, in addition to XPA, measuring the dielectric characteristics and SHG.

It was found that sintering of the $KNbO_3$ based ceramic from amorphous precursor and by the conventional ceramic method from crystalline oxides in a one-step heat-treatment regime occurs in a very narrow temperature interval of about about 5 – 10 K in the region 1040 – 1050°C. Above the optimal sintering temperature the samples melt, while with annealing temperature below 1030°C the samples remained porous and brittle irrespective of the type and quantity of the sintering additives. The compositions, heat-treatment regimes and properties of samples are presented in Table 2. The parameters of ceramic with a binder consisting of liquid alkali-silicate glass (LG) additions are also presented in Table 2.

The one-step sintering regime at 1040°C gives SHG signal values of about 5000 quartz standard units, which corresponds to a large uniform ceramic grain. However, a dense ceramic cannot be obtained in this case, while the porosity of the samples exceeds 15%.

The most densely sintered ceramic was obtained from the amorphous phase with a liquid potassium-silicate glass 4 wt.% (sample 4) by means of a two-step heat-treatment regime (700°C (4 h) + (1040°C (2 h)). The porosity of such a glass ceramic for the samples 3 and 4 did not exceed 5%.

GLASS CERAMIC MICROSTRUCTURE

A JSM 7500 FA JE scanning electron microscope was used to study the microstructure of sample 3 (Fig. 4).

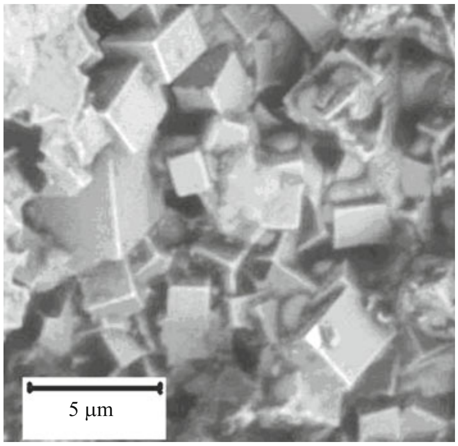

Fig. 4. Electron microscopic photograph of a section of a cleaved sample of glass ceramic from KNS-9.

Electron microscopy shows the presence of almost ideally formed cubic crystals of $KNbO_3$, whose flat faces can adjoin one another. The latter circumstance creates the best conditions for a uniform distribution of the electric field inside a material and maximizes its dielectric response, which manifested as unusually high for polycrystalline $KNbO_3$ values of the permittivity near the FE phase transition. The temperature of the FE phase transition of a $KNbO_3$ single crystal ($T_c = 410°C$) is close to the value of T_c of sample 3, determined by means of SHG and dielectric spectroscopy.

The same sample demonstrated a strong SHG signal, corresponding to the density a crystalline grain of potassium niobate, which is found, however, in an environment comprised of a alkali-silicate interlayer. Apparently, this environment forms a "jacket" around a crystalline grain and screens it to a certain extent from the laser radiation (SHG signal about 3000 in samples with liquid glass compared with the 5000 signal for pure crystalline $KNbO_3$ powder). A value of the SHG of about 3400 indicates that grain growth is limited by potassium-silicate glass interlayers formed at 700°C.

It can be supposed from the data in Table 2 that the jacket is formed during low-temperature annealing near 700°C and remains with subsequent heating in the interval 1000 – 1050°C, even though the crystalline state and morphology of the ceramic grain undergo significant changes at this temperatures.

EFFECT OF INTERCRYSTALLINE BINDER ON CERAMIC DIELECTRIC PROPERTIES

The dielectric permittivity data presented in Fig. 5 for the ferroceramic obtained are in agreement with the high perfection of the ceramic microstructure obtained. The dielectric properties of the ceramic samples were studied in the temperature interval $t = 20 – 570°C$ and frequency range 5 – 1000 kHz. The samples consisted of 2 – 3 mm high, 10 mm in diameter ceramic pellets. Platinum electrodes were deposited on the plane-parallel faces of the samples and then burned in at 700°C in 30 min. The heating rate of the samples was 10 K/min.

An important quality indicator of a dielectric material, specifically, a ferroceramic, is its capacity to accumulate electric energy without dissipating it in the form of heat. This property of the material is characterized by the tangent of the dielectric loss angle tan δ. The smaller tan δ, the better the electrical insulation is, i.e., the lower the value of $\sigma = \varepsilon\omega \tan\delta$ at frequency ù of the electric field.

It is interesting to compare the electric insulation properties of potassium niobate based ceramic, obtained by sintering from crystalline oxides with LiF additive and from amorphous precursor with permeation by liquid sodium-silicate glass, expressed in this manner (Fig. 6). It is important to note that the values of the tangent of the angle of dielectric losses and the dielectric permittivity for this ceramic depend

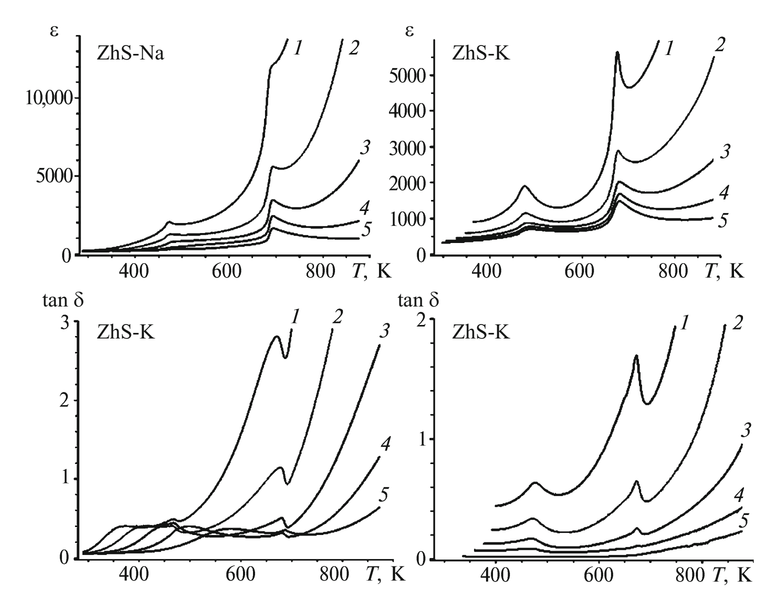

Fig. 5. Temperature dependences of the dielectric permittivity ε and tangent of the angle of dielectric losses tan δ for ferroceramic from KNS-9 glass with binder from sodium-silicate (LG-Na) or potassium-silicate (LG-K) glass at the frequencies 10 kHz (*1*), 30 kHz (*2*), 100 kHz (*3*), 300 kHz (*4*) and 1 MHz (*5*).

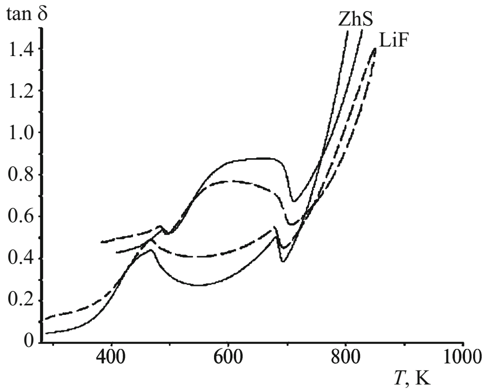

Fig. 6. Temperature dependence of the tangent of the angle of dielectric losses at the frequency 10 kHz in a heating–cooling cycle for $KNbO_3$ ceramic sintered with the addition of liquid glass (solid line) or LiF powder (dashed line).

TABLE 3. Characteristics of Ceramic with KNS-9 Composition and Different Sintering Additives at Frequency 100 kHz

Indicator	Ceramic	
	LG-Na	LG-K
ε	2400	1700
tan δ	0.4	0.08

strongly on the composition of the sintering additive (Table 3). It is evident that the $KNbO_3$ glass ceramic obtained by the glass ceramic technology differs beneficially from its conventional analog by low values of tan δ in the entire range of existence of the ferrophase (below 410°C), which determines its advantage for different applications.

The results obtained in the present work show that there is promise in the glass ceramic technology of potassium niobate based ferroelectric ceramic, which can be extended to niobate compounds with a more complicated composition of the perovskite type and compounds related to perovskite, which possess valuable combinations of properties.

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